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Composite materials for application on naval aircraft must possess certain unique characteristics including toughness, resistance to temperature and moisture, and high specific strength. One resin system being investigated for potential airframe applications is PETI-RFI; an addition polyimide developed at NASA/s Langley Research Center. Thermogravimetric analysis (TGI), modulated differential scanning calorimetry, (MDSC), and rheology measurements were used to determine the cure kinetics, glass transition temperature (T_g), processing temperatures, and thermal decomposition kinetics. The resin system was cured for 1 hr at 371°C, to ensure complete cure. Cure kinetics, based on the variable heating rate method, exhibit an activation energy of 164.5 kJ/mol (39.3 kcal/mol). The measured behavior agrees with work reported by Hinkley on similar phenylethynyl-terminated compounds. Decomposition kinetics were investigated in order to assess high-temperature performance limits. Useful lifetime plots were incorporated based on the Toop equation, which allows the lifetime predictions based on the rate of resin weight loss.

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THERMAL CHARACTERIZATION OF PETI-RFI FOR AIRCRAFT APPLICATIONS

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ABSTRACT

Composite materials for application on naval aircraft must possess certain unique characteristics including toughness, resistance to temperature and moisture, and high specific strength. One resin system being investigated for potential airframe applications is PETI-RFI; an addition polyimide developed at NASA's Langley Research Center. Thermogravimetric analysis (TGA), modulated differential scanning calorimetry (MDSC), and rheology measurements were used to determine the cure kinetics, glass transition temperature (T_g), processing temperatures, and thermal decomposition kinetics. The resin system was cured for one hour at 371°C, to ensure complete cure. Cure kinetics, based on the variable heating rate method, exhibit an activation energy of 164.5 kJ/mol (39.3 kcal/mol). The measured behavior agrees with work reported by Hinkley[4] on similar phenylethynyl-terminated compounds. Decomposition kinetics were investigated in order to assess high-temperature performance limits. Useful lifetime plots were incorporated based on the Toop[5] equation, which allows the lifetime predictions based on the rate of resin weight loss.

KEY WORDS: Thermal Analysis, Polyimide, Resin Transfer Molding

1. INTRODUCTION

High temperature organic matrix composite resins have not traditionally been candidates for resin transfer molding (RTM) due to their high melt viscosity and tendency to generate volatiles during cure (e.g. PMR-15). Material development for low-cost RTM processing is presently being pursued by a number of government and industrial groups. One system under consideration by the Navy is a phenylethynyl end-capped addition polyimide (PETI-5) developed at the NASA Langley Research Center. Previous work included utilizing a reactive

plastisizer to lower the overall viscosity of PETI-5[1]. Typical cure temperatures in excess of 375°C are required to fully process this class of addition polyimide. The plastisizer is incorporated into the network as the composite is cured without the release of toxic or volatile agents. Viscosity reduction has also been obtained by introducing flexibility into the polymer backbone eliminating the need for additives. This new material is called PETI-RFI. Thermal characterization of PETI-RFI was performed to quantify thermal stability and formulate processing guidelines. Thermogravimetric analysis (TGA), modulated differential scanning calorimetry (MDSC) and dynamic mechanical analysis (DMA) were used to characterize cure kinetics, glass transition behavior, and decomposition kinetics.

2. KINETICS METHODS

The variable heating rate method [2] was employed to obtain kinetic data by both the differential scanning calorimetry (DSC) and the thermogravimetric analyzer (TGA). The heating rates chosen were 0.2, 0.5, 1.0, 5.0, 10.0 and 20.0 °C/min. One equation was used for both the DSC and TGA for calculating the activation energy. The equation is,

$$\frac{d\log\beta}{d(1/K)} = 0.457E/R \qquad [1]$$

where, β is the heating rate, E is the activation energy, R is the gas constant (1.987 cal/molK), T is the absolute temperature, and the constant arises from the assumption of first-order behavior. A plot of the log-heating rate versus the reciprocal of the absolute temperature at a constant conversion will have a slope of 0.457 E/R. For DSC analysis, the constant conversion point is taken at the peak exotherm. While for TGA it is taken at constant weight loss, which ranged from 5 to 40% in this study. Thus, we have one activation energy for the DSC cure analysis and seven for the TGA decomposition analysis at various conversions. The Arrhenius frequency factor can be calculated from the equation,

$$A = \frac{\beta E}{RT^2} e^{\frac{E}{RT}} \qquad [2]$$

Once E and A are known, assuming a first order reaction, the rate constant, k, may be calculated from the equation,

$$\ln k = \ln A - \frac{E}{RT} \qquad [3]$$

3. DIFFERENTIAL SCANNING CALORIMETRY

3.1 CURE KINETICS The neat resin was run in a crimped aluminum pan in a nitrogen atmosphere with a flow rate of 50 ml/min. For each heating rate, Indium metal was used to calibrate the heat flow and onset temperature in the DSC cell. Figure 1 shows a typical DSC thermogram at a heating rate of 5°C/min for PETI-RFI powder as received from the NASA Langley Research Center. The resin has a glass transition at 142°C with the cure exothermic peak at 379.2°C and an enthalpy of cure of 153.5 J/g. With increasing heating rates, the exothermic cure peak shifts to a higher temperature. Table 1 lists the heating rates with their associated peak heights and total enthalpy values. Figure 2 is a plot of the log heating rate versus 1/K is for the six heating rates used. The straight line indicates that there is good

agreement with the assumption of first order behavior. The activation energy found was 164.5kJ/mol (39.3 kcal/mol) and the Arrhenius frequency factor was found to be 4.12x 10^{12} (1/min). Table 2 lists these kinetic data. These results are within good agreement with results reported by Hinkley[4] with phenylethynyl-terminated compounds. Listed in Table 3 are the rate constants at 360, 371, 380 and 400°C.

*3.2 **MDSC*** Modulated differential scanning calorimetry was performed using a TA Instruments model 2920 DSC. MDSC is a technique used to measure the heat flow between a sample and reference material as a function of time or temperature. In MDSC, a sinusoidally modulated heating rate is overlaid on the conventional heating rate. The net effect is a complex heating profile on the sample as if two experiments were being run at the same time. This can be represented by the following equation,

$$\frac{dQ}{dt} = C_p\beta + f(T,t) \qquad [4]$$

where $\frac{dQ}{dt}$ = the total heat flow, C_p is the heat capacity, β is the heating rate, and f(T, t) is the heat flow from the kinetic (absolute temperature and time dependent) processes. The instrument parameters used included a heating rate of 3°C/min with modulated temperature of ±1.0°C cycled every 60 sec. The MDSC analysis was performed in order to measure the glass transition temperatures (T_g), heat capacity, and residual cure peaks for PETI-RFI. Table 3 lists the specific heat capacity at 200 and 300°C. For the glass transition measurement, the neat uncured material was heated to 371°C at a heating rate of 3°C/min and then held for 1 hour to allow to for cure. The sample was control cooled at 10°C/min to room temperature then reheated again at 3°C/min to 400°C. Using this heat/cool/heat method, the sample T_g was measured with each step. In the first heating cycle the PETI-RFI exhibits a T_g of 145°C, after the 1 hour hold, the controlled cool down the T_g has increased to 242°C. The second heating shows that the T_g is stabilized at 247°C which indicates the PETI-RFI is fully cured.

4. TGA DECOMPOSITION KINETICS

A TA Instruments model 2950 TGA was used to analyze the thermal degradation of PETI-RFI. Isothermal and dynamic-temperature experiments were performed in a nitrogen atmosphere at a flow rate of 50 ml/min. For the isothermal experiment, four temperatures were selected (500, 450, 425, and 400°C) to obtain a weight loss of at least 5% for the kinetic analysis. All samples were fully cured before testing. Figure 3 shows the weight changes at the chosen temperatures. The percent weight change was calculated from weight change versus time information. The Arrhenius plot of the Log rate % min^{-1} versus the reciprocal of the absolute temperature was obtained, as shown in Figure 4. Since the behavior is linear, the assumption of first-order kinetic decomposition is valid. An activation energy of 162.6 kJ/mol (34.09 kcal/mol) was obtained.

Using the variable heating rate method, Figure 5 shows the TGA weight loss for each heating rate experiment. The curves are displaced to the right indicating higher temperatures as the heating rates increases assuming a first order reaction. Constant percent conversions from 5.0

to 40% are also shown. Table 5 lists the activation energies and pre-experiential factors for these conversions. The activation energies for both isothermal and variable heating-rate experiments are in close agreement which indicates that the same decomposition mechanism may apply in each case.

The relationship between time-to-conversion versus temperature is shown in Figure 6. This is an estimate of how long will it take the neat resin to lose 1, 5, 10 and 20% of the sample mass at various temperatures. Based on a 5% conversion, with an activation energy of 189.3 kJ/mol at 255°C, this material will lose 1% of its weight in 2.27 years.

An estimated service lifetime plot using a 5% conversion is shown in Figure 7. The plot illustrates the relationship between activation energy, estimated useful lifetime of the resin at any given percent conversion, and temperature. Toop[4] described this behavior with the following equation,

$$\ln t_f = \frac{E}{RT_f} + \ln\left[\frac{E}{\beta R} p \frac{E}{RT_C}\right] \qquad [5]$$

where, t_f is estimated time to failure, T_f = failure temperature (K), P = value from a numerical integration table, and T_c is the temperature from an operator selected weight loss (i.e. 2-5% at a selected heating rate). By developing such a chart, the useful life of a resin can be estimated. In the present study, PETI-RFI can maintain a useful lifetime at temperature up to 275°C.

5. MELT RHEOLOGY

Conventional resin transfer molding involves the infiltration of a fiberous reinforcement with a liquid matrix resin. To determine the applicability of PETI-RFI for RTM, two parallel-plate rheology experiments were performed with a Rheometrics model ARES rheometer. In each case, dry uncured power was cold sintered into 25-mm diameter disks and then placed between the aluminum platens. In the first experiment, the temperature was raised to 200°C prior to shearing the material. The sample was heated at 5°C/min while applying a 5% strain at 10 rad/s to obtain the complex viscosity behavior shown in Figure 8. The viscosity dropped quickly and remained relatively low until the sample began to cure rapidly at 320°C.

The second experiment intended to investigate the isothermal behavior to ensure the viscosity would remain low during long infiltration times. Similar uncured samples were rapidly heated to either 250, 275, 300, or 325°C and then monitored with 5% strain at 10 rad/s for three hours, as shown in Figure 9. The resulting behavior indicates a very stable viscosity for low temperatures with expected increases as the test temperature apporaches the cure temperature of the phenylethynyl end-cap. The isothermal and dynamic viscosity behavior indicate PETI-RFI is suitable for conventional RTM or resin film infiltration.

6. CONCLUSIONS

Thermal analysis data reveals that the PETI-RFI resin system is an excellent candidate for high temperature aerospace applications. The low minimum viscosity and short cure times allow for

this resin system to be used for RTM processes. MDSC evidence shows the cured resin T_g is 247°C. Thermal stability, as measured by TGA, verifies the high temperature applicability. Using the Toop equation, the material should last for more than a century at temperatures below 250°C with less than a 5% weight loss.

7. REFERENCES

1. Claus, S.J., Cramer, R.J., Smith, J., and Connell, J., "Thermal Properties of LaRC PETI-5™/Reactive Additive Blends," High Temple Workshop XVII, Naval Postgraduate School, Monterey, CA, Feb. 10-13, 1997.
3. ASN/ASTM E-698-79
4. J.A. Hinkley Journal of Advanced Materials.,vol 27,3 55 April (1996)
5. D.J. Toop, IEE Trans.Elec. Ins E-1-6, 2 (1971)

TABLE 1
DSC VARIABLE HEATING RATE DATA OF UNCURED PETI-RFI

HEATING RATE (°C/MIN)	PEAK HEIGHT (°C)	ENTHALPY (J/g)
0.2	318.5	116.1
0.5	333.5	144.5
1.0	348.0	151.7
2.0	364.5	158.3
5.0	379.3	153.5
10.0	379.7	159.9

TABLE 2
DSC CURE KINETICS DATA

ACTIVATION ENERGY (kJ/mol)	164.5
FREQUENCY FACTOR LOG A (1/min)	12.617

TABLE 3
RATE CONSTANTS FOR CURE KINETICS

TEMPERATURE (°C)	RATE CONSTANT (1/min)
360	$1.1 X10^{-1}$
371	$1.2 X10^{-1}$
380	$2.8 X10^{-1}$
400	$7.1 X10^{-1}$

TABLE 4
MDSC HEAT CAPACITY DATA OF CURED PETI-RFI

RUN NUMBER	C_P @ 200°C (J/g°C)	C_P @ 300°C (J/g°C)
1	1.644	2.071
2	1.994	2.169
3	1.886	2.364
4	1.591	1.957
5	1.673	2.105
AVERAGE	*1.758*	*2.133*

TABLE 5
KINETIC PARAMETERS AT DIFFERENT CONVERSION LEVELS

CONVERSION LEVEL (%)	ACTIVATION ENERGY (kJ/mol)	Log Pre-exp Factor (1/min)
5	189.3	10.65
10	198.1	11.01
20	217.2	12.19
25	228.9	12.92
30	241.9	13.72
35	255.3	14.53
40	267.4	15.24

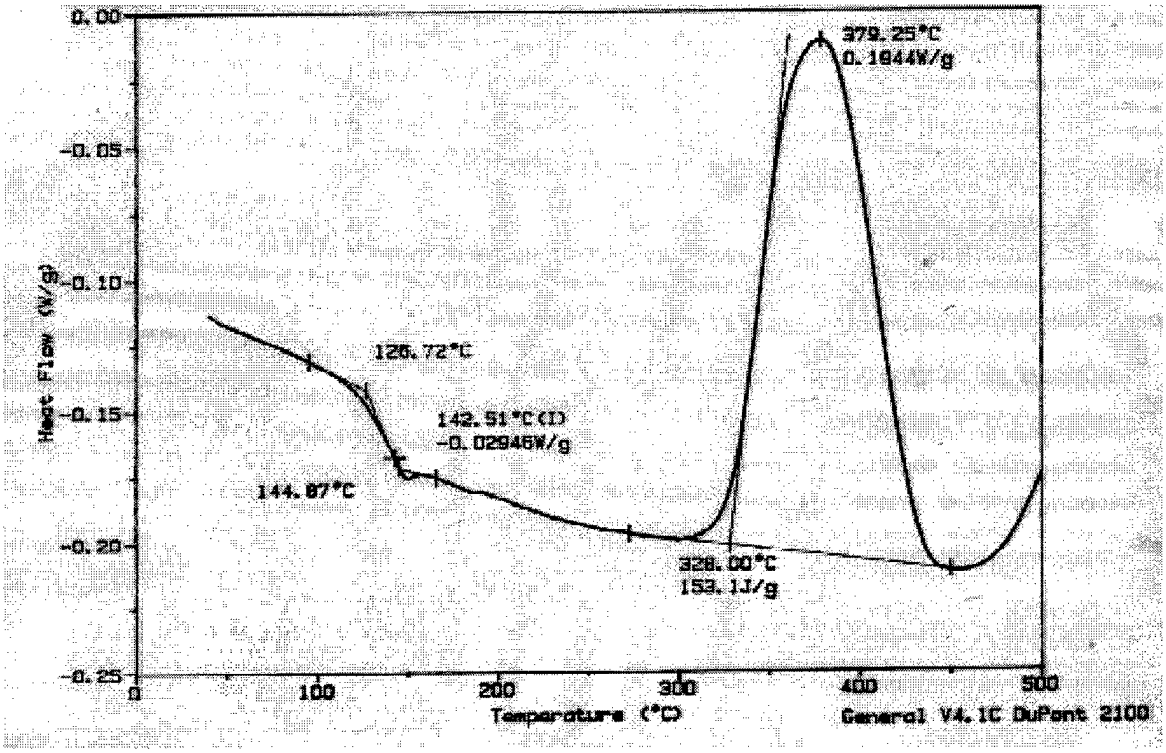

Figure 1. DSC curve of uncured PETI-RFI at 5°C/min.

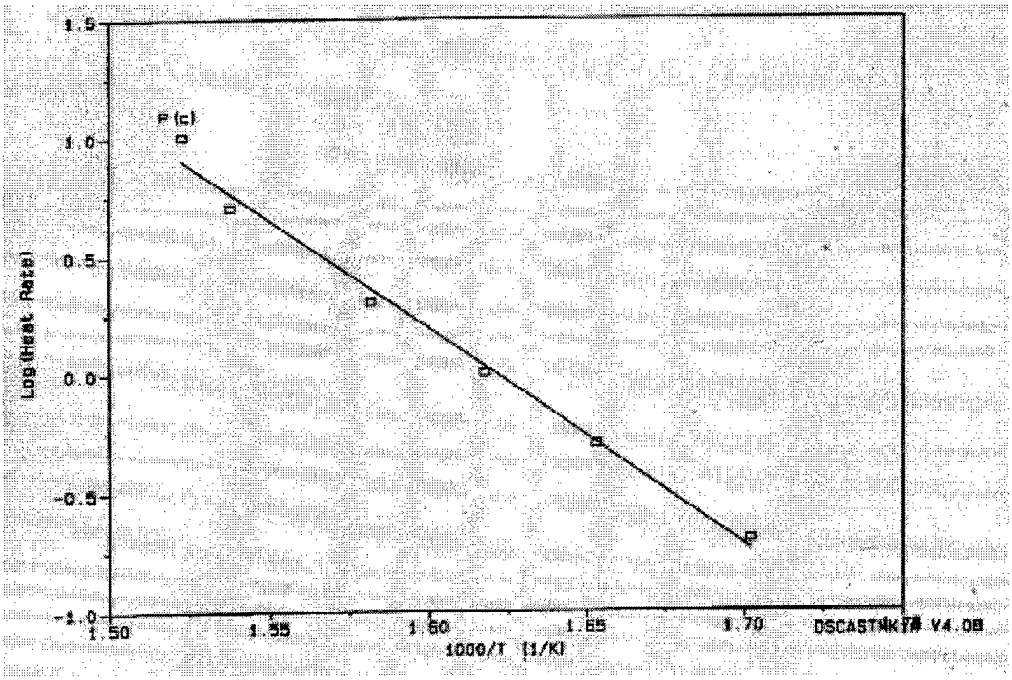

Figure 2. Arrhenius plot of DSC cure kinetics.

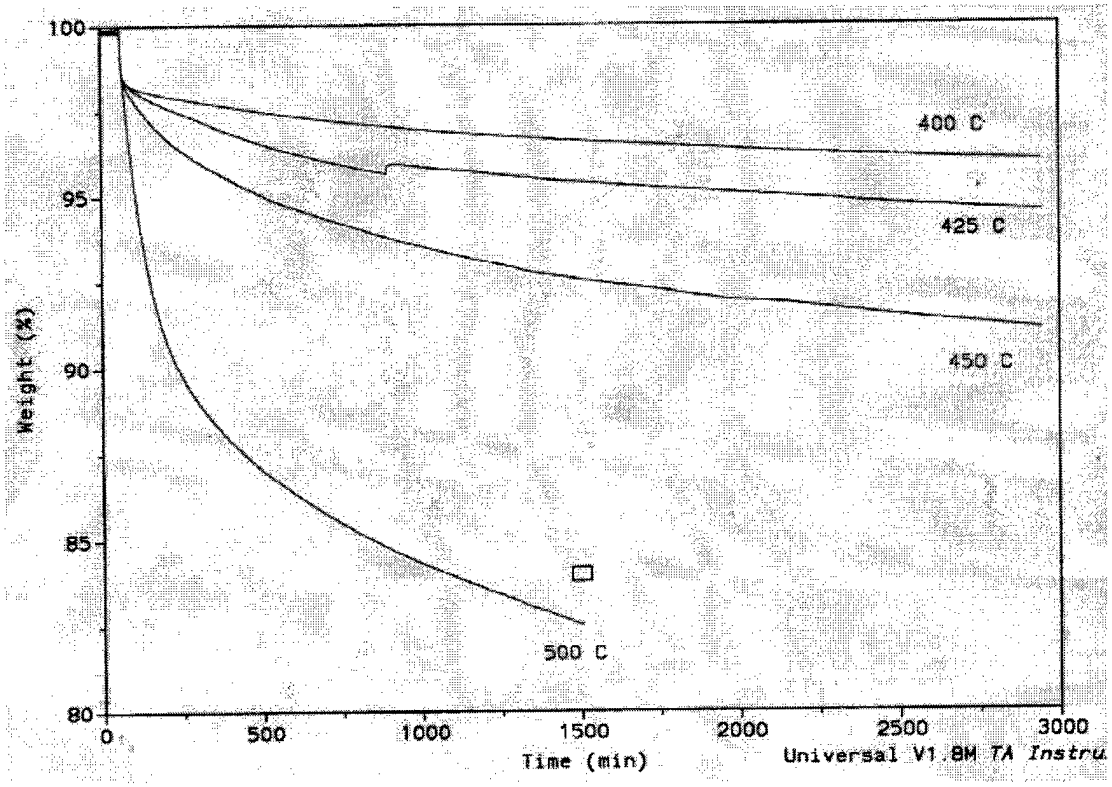

Figure 3. Isothermal TGA of weight changes at various temperatures.

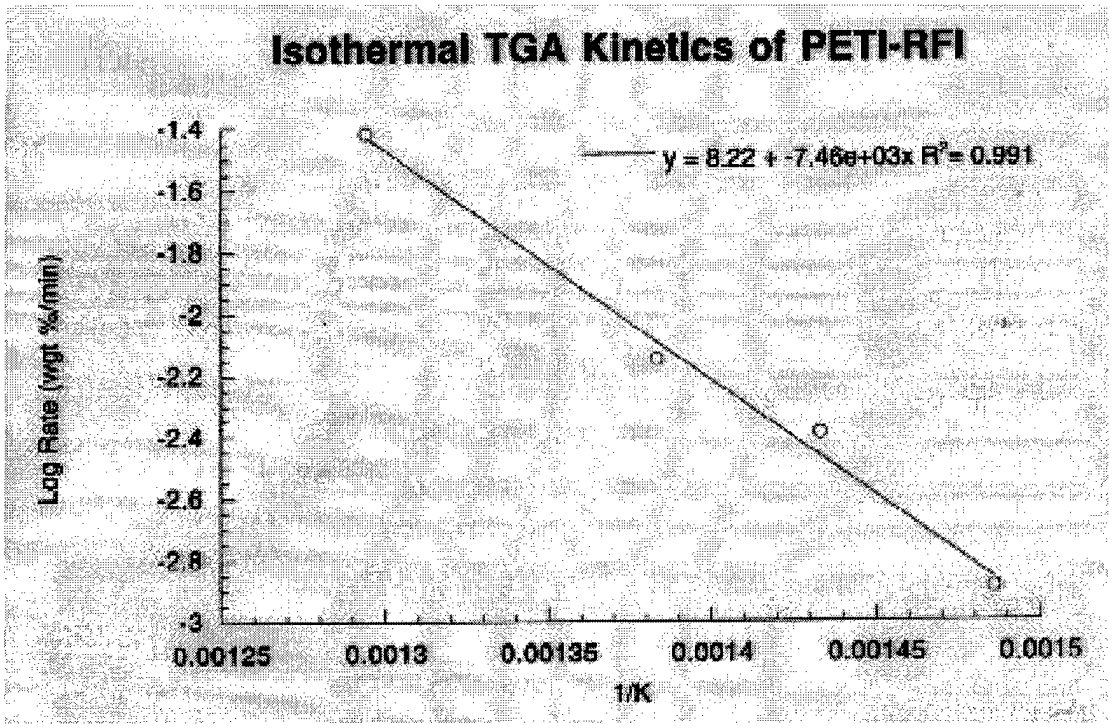

Figure 4. Arrhenius plot of isothermal TGA kinetics.

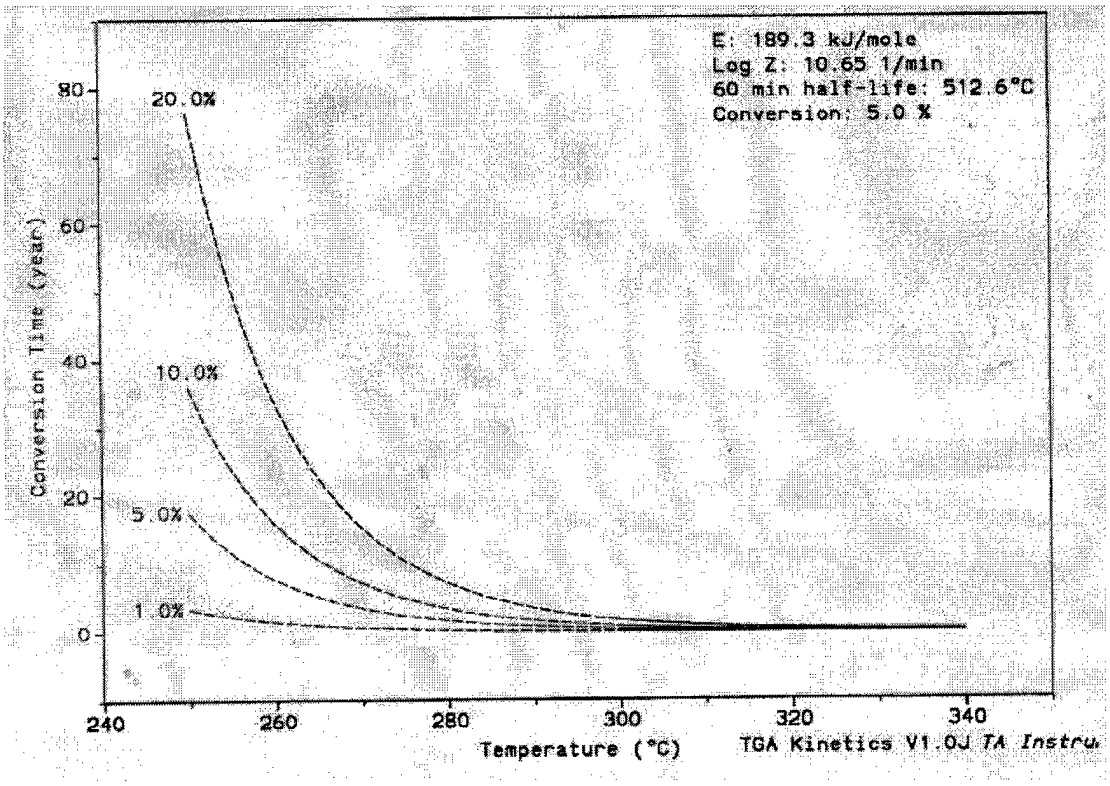

Figure 5. Time to conversion versus temperature at a 5% conversion.

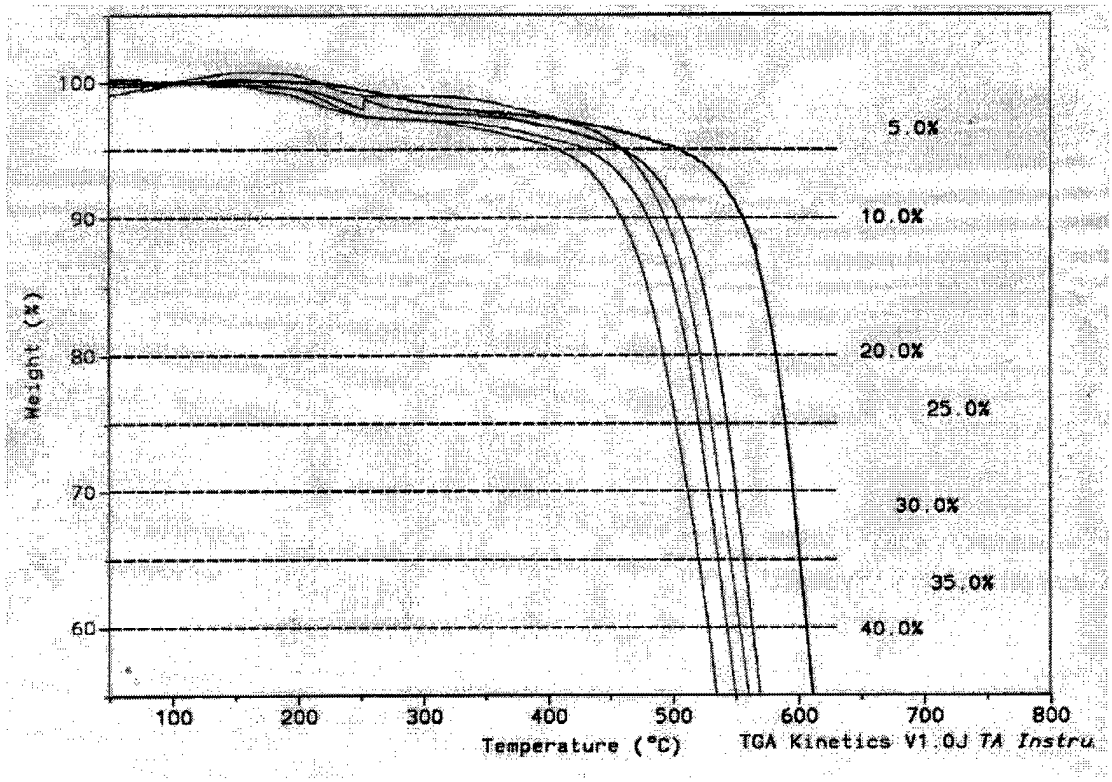

Figure 6. TGA variable heating rates of PETI-RFI decomposition.

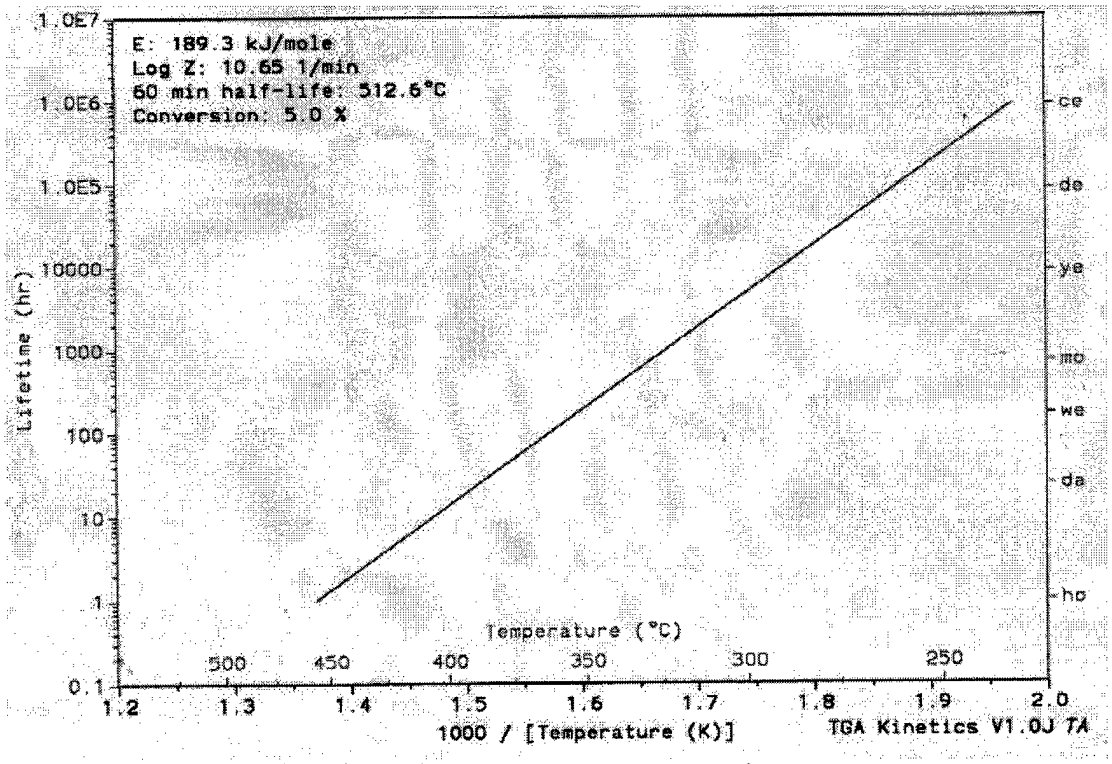

Figure 7. Life-time plot of cured PETI-RFI at 5% conversion.

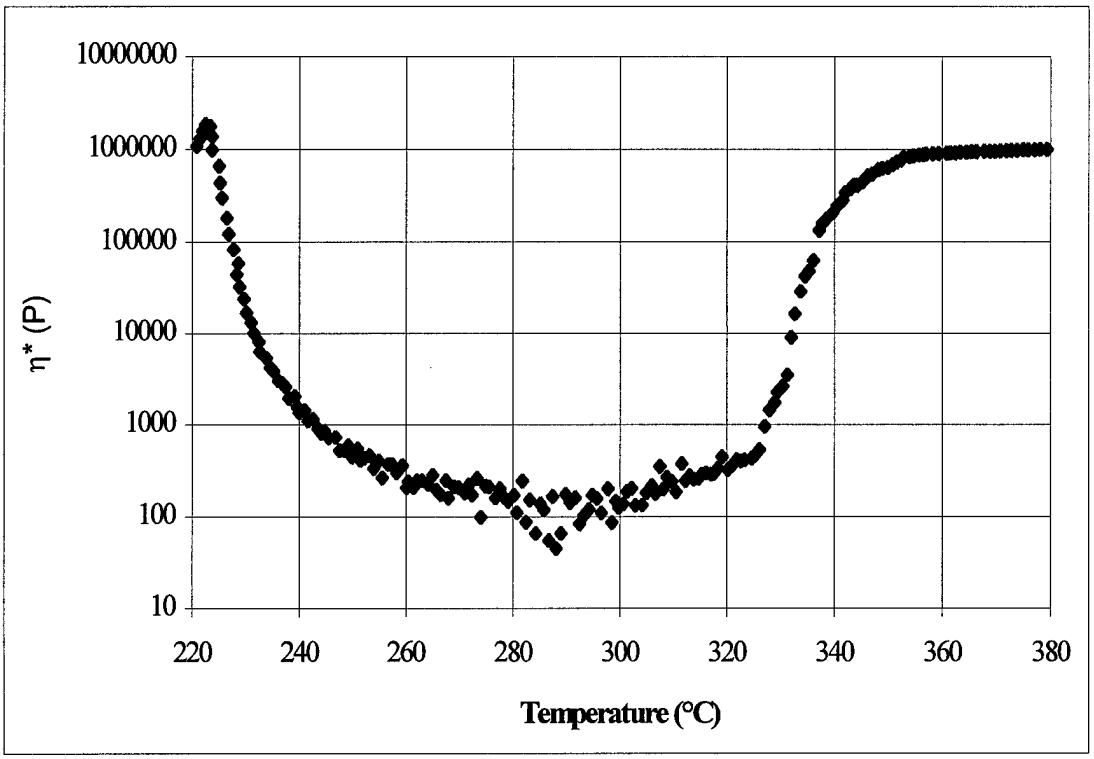

Figure 8. Complex viscosity of PETI-RFI during heating at 5°C/min.

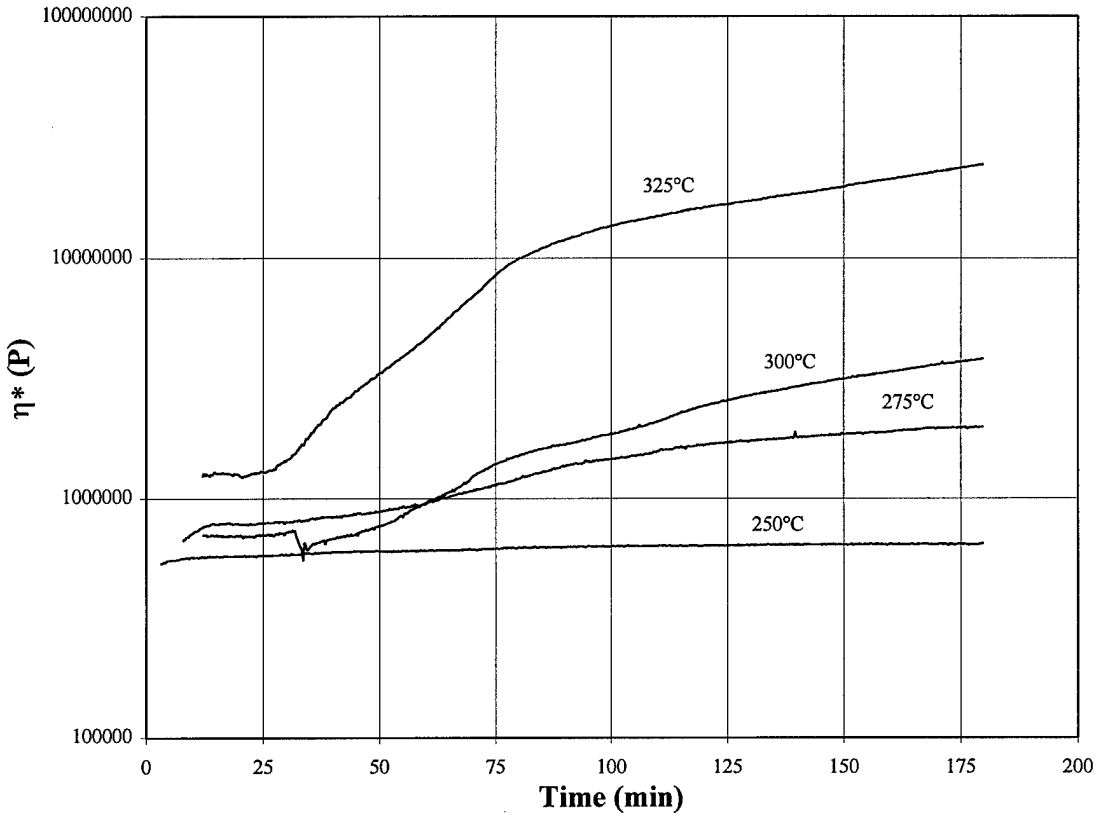

Figure 9. Isothermal complex viscosities of PETI-RFI at various temperatures.